Metasomatising the lunar mantle with TiO₂-rich melts: A disequilibrium porous flow model. A. R. Beck, P. C. Hess, and Y. Liang Brown University Department of Geological Sciences, 324 Brook St, Providence RI, 02912 U.S.A. Alyssa Beck@brown.edu

Introduction: The picritic glass beads, found at every Apollo sampling site, have the most primitive compositions among the lunar volcanic rocks [1,2]. Even though these glasses have undergone a certain degree of shallow level olivine crystallization, the bulk of the lunar volcanic glass suite can be acceptably modeled as the partial melting products of an olivine + orthopyroxene source region deep within the lunar mantle [3]. Interestingly, the melts are all undersaturated with respect to ilmenite (and clinopyroxene) at all pressures thus investigated [4,5]. A source region of primitive LMO olivine and orthopyroxene, even when melted in small degrees cannot account for these compositions. A TiO2-enriched source is required to explain basalts with higher TiO₂ contents. Among the models proposed include the overturn model [6], which predicts that the cumulate pile must redistribute itself. The gravitationally unstable, Fe-Ti rich cumulates sink deep into the lunar mantle, displacing the more Mg-rich crystals to shallower levels. This is an appealing model, as it provides the lunar mantle with an infusion of incompatible heat producing elements that may provide heat needed to instigate partial melting at depth.

Elkins-Tanton et al, [7] modeled cumulate overturn in the LMO and found that redistribution of the solid ilmenite cumulate layer was unlikely due to the high viscosity of the layer at the temperatures investigated. They proposed instead that the most feasible mechanism for sinking the high TiO₂ material was to re-melt the clinopyroxene and ilmenite cumulate layer through radiogenic or shock heating. This would create ilmenite rich liquids which are significantly denser than the underlying mantle, and could sink into and fertilize the mantle.

In order to further explore the overturn models [6,7] we compare the geochemical consequences of sinking a solid ilmenite-bearing layer and downward percolation of a TiO2-rich liquid into the underlying cumulates. Solid-state overturn will result in simple mechanical mixing between the ilmenite-rich rocks and the underlying cumulates. Downward percolation of a TiO2-rich melt through a porous cumulate pile will inevitably lead to melt-rock reaction because the through-going melt is not in chemical equilibrium with its host matrix. One of the widely recognized features of melt-rock reaction in a porous rock is the chromatographic fractionation among the compatible and incompatible elements [8,9]. Due to their smaller crystal-melt partition coefficients and finite crystalmelt exchange rates, the highly incompatible elements have an effectively larger percolation velocity than the more compatible elements. Hence it is quite possible to distinguish source regions that experienced mechanic mixing or melt-rock reaction from their compatible and incompatible element compositions

Model: To illustrate the chromatographic effects we solve a simple 1D diffusion-advection-reaction equation for both the descending liquid and the host solid it modifies for 4 selected elements (TiO2, Al2O3, CaO, and Cr₂O₃). The descending ilmenite-rich melts are relatively rich in CaO and TiO₂ compared to the cumulate olivine and orthopyroxene. CaO and TiO₂ are incompatible in these two phases. Al₂O₃ is only slightly more compatible in orthopyroxene at high pressures. Cr is compatible in orthopyroxene. Modeling the behavior of these elements during porous flow should provide insight into the liquid's ability to fertilize the deep, picritic glass source region. For purpose of illustration we assume that the initial compositions of the mantle phases are uniform throughout the column, constant percolation velocity and constant melt porosity in the host matrix (5%). Partition coefficients (Kd) are taken from [10,11]. Diffusion coefficients in the liquid are from [12] and diffusion coefficients in the solid phase are from a variety of sources in the literature. Due to a dearth of data, we use estimates for some elements in orthopyroxene and olivine based on literature values for clinopyroxene [14].

Results: Models we have run include a descending cpx-ilm melt which has TiO₂ and CaO contents of 17 wt % each and Al₂O₃ of 3%. This is comparable to the 33% ilmenite, 66% clinopyroxene used in [7]. Figures 1a and 1b show the calculated concentration profiles of the four elements in the interstitial melt and the host matrix, respectively. In the liquid, trace element concentrations are initially higher than in the solid (except for Al₂O₃). Over time, the liquid migrates downward, and loses some TiO2, CaO and Cr₂O₃ to the solid. Because TiO₂ has a much slower diffusion rate, the liquid descends hundreds of kilometers with minimal modification of the solid's TiO₂ content. The solid residue gains less than 0.2% TiO₂. The CaO concentration front is greatly decoupled from that of TiO2, as it is more compatible in orthopyroxene, and the diffusion rate for the 2⁺ cation is much faster than that of Ti⁴⁺. The liquid has become highly depleted in CaO by 200 km depth (x/L = 2 in fig 1a). The top 50 km of the solid have fully equilibrated with the initial liquid at t = 5 Ma. Al³⁺ has a slower exchange rate than Ca²⁺, but this is offset

somewhat by its higher Kd in orthopyroxene The liquid gains Al₂O₃ as it reacts with the solid. The effect on Cr is striking; Cr₂O₃ is more compatible and also has a faster diffusion rate, which leads to very rapid equilibration. The liquid is depleted in Cr₂O₃ in less than 50km. Modification of the column begins at the top and moves down over time. The elements with higher reaction rates and higher Kds are effectively decoupled from TiO₂. The solid composition adjusts much more slowly than the fluid, as it is limited by solid-state diffusion.

We can use simple melting models to compare the liquids produced by partial melting to the actual picritic glasses. Several distinct chemical trends within the picritic glass suite are addressed including the spectrum of TiO2 contents, decreasing CaO and Al₂O₃ with increasing TiO₂. Fig. 2 is a ternary plot that displays 1% and 10% partial melts from the solid column of 1b. These melts do not resemble the actual suite of picritic glasses. The descending melt did not impart enough TiO2 to the solid, and melt-rock reactions effectively slowed the velocity of the CaO and Cr₂O₃ concentration fronts such that deeper source regions did not become enriched in these components. Additional arguments which do not favor the natural picritic glasses having experienced reactive porous flow during their later ascent include their increased Cr₂O₃ content with increasing TiO₂ content. The positive correlation is not consistent with the decoupling shown in Fig 1a. The negative Eu anomalies seen in the high Ti glasses are also difficult to preserve during porous flow as Eu²⁺ tends to fractionate from the other REEs, which are 3⁺ cations (see [15]).

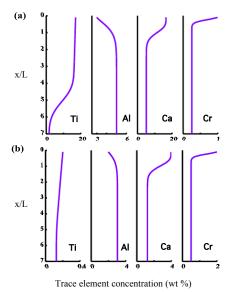


Figure 1. "Metasomatism" of a solid mantle column via reactive porous flow after t = 5 Ma. x/L represents depth in the column and one unit of x/L = 100 km. Melt velocity is 10 cm/yr. (a) represents the liquid composition. The composition of the initial descending liquid can be read at x/L = 0, and initial interstitial liquid at x/L = 7. (b) represents the solid composition. x/L = 7 is the initial solid

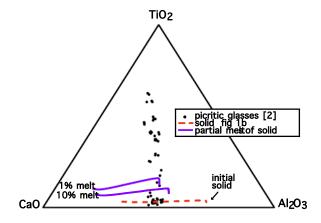


Figure 2. Comparison of calculated melt compositions produced by 1% and 10% partial melting of the metasomatised source region shown in Fig 1b, with picritic glasses from [2]. For reference, the solid composition is shown as a dashed line. The descending melt has enriched the mantle in CaO, but TiO₂ was relatively unchanged. As shown in this figure, chromatographic fractionation alone is incapable of producing the source region for the picritic glasses.

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